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Stark effect : a simple approach by perturbative method

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Abstract : An elegant method using perturbation theory in the parabolic coordinate representation has been developed for an exhaustive study of the Stark effect in hydrogenic atoms which can provide eigenenergy as well as eigenfunctions to all orders in external field intensity. As an application, the energy and eigenfunction expansions for the perturbation of a hydrogen atom to fourth order have been calculated. It has been noticed that these different order term values of eigenenergy tally exactly with previous calculations

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1. Introduction

The theoretical investigation of the Stark effect in atomic hydrogen has started its journey from the days of old quantum theory [1] and since the early works [2] in the beginning of the new quantum theory the Stark problem has received almost continuous attention [3] till recent times [4]. A number of workers deal with the perturbation expansion of the energy to different higher orders [5–7] while the construction of higher order explicit perturbed wave functions seem to fail to draw such attention though Mandelsohn [8] in his extensive work on the ground state of a one-electron ion obtained both the energy and the wave function explicitly through tenth order.

In a recent work [9] where excitation of the hydrogen atom from ground state to $n = 2$ level by electron impact in the presence of a laser field has been dealt with, we have constructed the first order dressed wave functions of the target perturbed by a harmonic electric field assuming the states to be quasistationary. For the study of higher order effects of such processes we need some straightforward method which can provide higher order explicit

wave functions as well as energy corrections in a systematic way. With this end in view, we develop in the present paper, an elegant method which can account for the Stark effect of a hydrogen-like atom by uniform electric field to all orders of perturbation. We also consider application of the general theory to neutral hydrogen atom for the construction of the eigenfunctions and calculation of the energy corrections up to fourth-order with respect to the external field intensity.

It should be pointed out that the Stark state is not a proper bound state but simply a quasibound state which ultimately decays. As a result the normalisation integral should diverge. However, this quasibound state may be considered as a 'stationary' state to all intents and purposes which can be normalised in its appropriate domain. The justification is as follows.

For an H atom placed in a uniform field 'F ' along z-direction, the potential energy is $\left(-Ze^2/r + Fz\right)$. There is some large negative value of z for which the potential energy is equal to the total energy E and beyond this the electron can move freely to $-\infty$. Thus, the uniform field provides a potential barrier through which the electron can tunnel from the region near the origin to the region near $z = -\infty$. Therefore, strictly speaking, the quantised states near the origin are not permanently stationary states. However, the potential barrier will be very thick for a relatively weak field *i.e.* the probability of ionisation is vanishingly small. In this case the electron will take an extremely long time to leak out and as a result the energy states will be practically stationary.

2. Theory

The Schrödinger equation for a hydrogen-like atom in a constant homogeneous external electric field of strength $\mathcal{E}$ is given (in atomic units) by

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \mathcal{E}z\right]\Psi = E\Psi. \tag{1}$$

Here the electric field is assumed to be along the z-axis.

It is well known that for a hydrogen atom in a uniform electric field the separation of variables in Schrodinger equation is possible in parabolic coordinates and this fact has been utilised here conveniently. So defining the parabolic coordinates ξ, η, ϕ as

$$\xi = r+z, \quad \eta = r-z, \quad \phi = \tan^{-1}(y/x), \tag{2}$$

and assuming Ψ to be of the form

$$\Psi = F_1(\xi)\, F_2(\eta)\, \exp(\mathrm{i}m\phi), \tag{3}$$

m being the magnetic quantum number, we obtain the following equations for F_1 and F_2 :

$$\frac{d}{d\xi}\left(\xi\frac{dF}{d\xi}\right) + \left(\frac{1}{2}E\xi + Z\beta_1 - \frac{m^2}{4\xi}\right)F_1 = \frac{\mathcal{E}}{4}\xi^2 F_1, \tag{4}$$

$$\frac{d}{d\eta}\left(\eta\frac{dF}{d\eta}\right) + \left(\frac{1}{2}E\eta + Z\beta_2 - \frac{m^2}{4\eta}\right)F_2 = -\frac{\mathcal{E}}{4}\eta^2 F_2, \tag{5}$$

Here the separation parameters β_1 and β_2 are related by

$$\beta_1 + \beta_2 = 1. \tag{6}$$

In order to solve eqs. (4) and (5) by the method of perturbation, we write

$$F_1 = \sum_{i=0}^{r} \lambda^i f_i \; ; \quad F_2 = \sum_{i=0}^{r} \lambda^i g_i \; ; \quad E = \sum_{i=0}^{r} \lambda^i E_i \; ,$$

$$\beta_1 = \beta_{10} + \sum_{i=1}^{r} \lambda^i b_i \; ; \quad \beta_2 = \beta_{20} - \sum^{r} \lambda^i b_i, \tag{7}$$

where $\lambda = \mathcal{E}$. In the above equation, β_1 and β_2 have been chosen in that manner so that condition (6) is satisfied. It has seen later that this particular choice simplifies the calculations to a great extent manifesting the elegance of the method.

Substituting eq. (7) in eqs. (4) and (5) and equating the coefficients of λ^i from both sides we get the following sets of equations :

$$\frac{d}{d\xi}\left(\xi\frac{df_i}{d\xi}\right) + \left(\frac{1}{2}E_0\xi + Z\beta_{10} - \frac{m^2}{4\xi}\right)f_i = \left(\frac{1}{4}\xi^2 - \frac{1}{2}E_1\xi - Zb_1\right)f_{i-1}$$

$$- \sum_{k=0}^{i-2}\left(\frac{1}{2}E_{i-k}\xi + Zb_{i-k}\right)f_k, \tag{8}$$

$$\frac{d}{d\eta}\left(\eta\frac{dg_i}{d\eta}\right) + \left(\frac{1}{2}E_0\eta + Z\beta_{20} - \frac{m^2}{4\eta}\right)g_i = \left(-\frac{1}{4}\eta^2 - \frac{1}{2}E_1\eta + Zb_1\right)g_{i-1}$$

$$- \sum_{k=0}^{i-2}\left(\frac{1}{2}E_{i-k}\eta - Zb_{i-k}\right)g_k. \tag{9}$$

We now introduce in place of E_0, ξ, η the quantities

$$n = \frac{Z}{\sqrt{-2E_0}} \; ; \quad \rho_1 = \xi\sqrt{-2E_0} = \xi Z/n; \quad \rho_2 = \eta Z/n. \tag{10}$$

With these transformations eqs. (8) and (9) become

$$\frac{d^2 f_i}{d\rho_1^2} + \frac{df_i}{d\rho_1} + \left(-\frac{1}{4}\rho_1 + n\beta_{10} - \frac{m^2}{4\rho_1}\right)f_i = \left(\frac{n^3}{4Z^3}\rho_1^2 - \frac{n^2}{2Z^2}E_1\rho_1 - nb_1\right)f_{i-1}$$

$$- \sum_{k=0}^{i-2}\left(\frac{n^2}{2Z^2}E_{i-k}\rho_1 + nb_{i-k}\right)f_k, \tag{11}$$

$$\rho_2 \frac{d^2 g_i}{d\rho_2^2} + \frac{dg_i}{d\rho_2} + \left(-\tfrac{1}{4}\rho_2 + n\beta_{20} - \frac{m^2}{4\rho_2} \right) g_i = \left| -\frac{n^3}{4Z^3}\rho_2^2 \right.$$

$$- \frac{n^2}{2Z^2} E_1 \rho_2 + nb_1 \Big) g_{i-1} - \sum_{k=0}^{i-2} \left(\frac{n^2}{2Z^2} E_{i-k}\rho_2 - nb_{i-k} \right) g_k \qquad (12)$$

Let us consider eq. (11) with $i = 0$ which may be written as

$$\frac{d^2 f_0(\rho_1)}{d\rho_1^2} + \frac{1}{\rho_1} \frac{df_0(\rho_1)}{d\rho_1} + \left(-\frac{1}{4} + \frac{n}{\rho_1}\beta_{10} - \frac{m^2}{4\rho_1^2} \right) f_0(\rho_1) = 0. \qquad (13)$$

The behavior of $f_0(\rho_1)$ in the asymptotic region ($\rho_1 \to \infty$) and near the origin ($\rho_1 \to 0$) suggests that we should search for a solution to eq. (13) of the form

$$f_0(\rho_1) = \exp(-\rho_1/2)\, \rho_1^{|m|/2}\, \omega_{1,0}(\rho_1), \qquad (14)$$

where $\omega_{1,0}(\rho_1)$ satisfies the following differential equation

$$\rho_1 \omega''_{1,0}(\rho_1) + (|m| + 1 - \rho_1)\, \omega'_{1,0}(\rho_1) + n_1 \omega_{1,0}(\rho_1) = 0, \qquad (15)$$

with

$$n_1 = n\beta_{10} - (|m|+1)/2. \qquad (16)$$

In eq. (15) $\omega''_{1,0}(\rho_1)$ and $\omega'_{1,0}(\rho_1)$ denote respectively, the first and second order derivatives of $\omega_{1,0}(\rho_1)$ with respect to ρ_1.

The regular solution of eq. (15) is the well-known associated Laguerre polynomial

$$\omega_{1,0}(\rho_1) = L^{|m|}_{n_1+|m|}(\rho_1), \qquad (17)$$

where n_1 must be a non-negative integer.

In view of the form of the zeroth order solution $fo(\rho_1)$ [eq. (14)] the solution to the eq. (11) may be written as

$$f_i(\rho_1) = \exp(-\rho_1/2)\, \rho_1^{|m|/2}\, \omega_{1,i}(\rho_1), \qquad (18)$$

which gives us the differential equation for $\omega_{1,i}(\rho_1)$

$$\rho_1 \omega''_{1,i}(\rho_1) + (|m| + 1 - \rho_1)\, \omega'_{1,i}(\rho_1) + n_1 \omega_{1,i}(\rho_1)$$

$$\frac{n^3}{4Z^3}\rho_1^2 - \frac{n^2}{2Z^2} E_1 \rho_1 - nb_1 \Big| \omega_{1,i-1}(\rho_1)$$

$$\sum_{k=0}^{i-2} \left(\frac{n^2}{2Z^2} E_{i-k}\rho_1 + nb_{i-k} \right| \omega_{1,k}(\rho_1). \qquad (19)$$

The first order solution of the above equation, $\omega_{1,1}(\rho_1)$, involves on the right hand side $\omega_{1,0}(\rho_1)$ which is the Laguerre polynomial $L^{|m|}_{n_1+|m|}(\rho_1)$ [see eq. (17)].

Now, the associated Laguerre polynomials satisfy the recurrence relations

$$x\,L^{|m|}_{p+|m|}(x) = \sum_{h=-1}^{+1} H_p(h)\; L^{|m|}_{p+|m|+h}(x), \tag{20}$$

with

$$H_p(1) = -\frac{p+1}{p+|m|+1},\quad H_p(0) = 2p+|m|+1,\quad H_p(-1) = -(p+|m|)^2, \tag{21}$$

and

$$x^2\,L^{|m|}_{p+|m|}(x) = \sum_{l=-2}^{+2} C_p(l)\; L^{|m|}_{p+|m|+l}(x), \tag{22}$$

with

$$C_p(2) = \frac{(p+1)(p+2)}{(p+|m|+1)(p+|m|+2)},\quad C_p(1) = -\frac{2(p+1)(2p+|m|+2)}{(p+|m|+1)},$$

$$C_p(0) = 6p^2 + 6p|m| + 6p + |m|^2 + 3|m| + 2,$$

$$C_p(-1) = -2(p+|m|)^2(2p+|m|),\quad C_p(-2) = (p+|m|)^2(p+|m|-1)^2. \tag{23}$$

In view of eqs. (17), (20) and (22), the right hand side of eq. (19) with $i = 1$ suggests writing $\omega_{1,1}(\rho_1)$ as

$$\omega_{1,1}(\rho_1) = \sum_{j=-2}^{2} R_1^{(1)}(j)\; L^{|m|}_{n_1+|m|+j}(\rho_1). \tag{24}$$

In the same way for the general solution of the eq. (19), we can write

$$\omega_{1,i}(\rho_1) = \sum^{+2i} R_1^{(i)}(j)\; L^{|m|}_{n_1+|m|+j}(\rho_1). \tag{25}$$

The coefficients $R_1^{(i)}(j)\,[-2i \le j \le 2i]$ can be determined by substituting eq. (25) in eq. (19) and equating the coefficients of $L^{|m|}_{n_1+|m|+j}(\rho_1)$ from the both sides of the equation. Thus, we get

$$-jR_1^{(i)}(j) = \frac{n^3}{4Z^3}\sum_{l=-2}^{+2} R_1^{(i-1)}(j+l)C_{n_1+j+l}(-l) - n\sum_{k=0}^{i-1} b_{i-k}R_1^{(k)}(j)$$

$$-\frac{n^2}{2Z^2}\sum_{k=0}^{i-1} E_{i-k}\sum_{h=-1}^{+1} R_1^{(k)}(j+h)\,H_{n_1+j+h}(-h), \tag{26}$$

from where $R_1^{(i)}(j)$'s can easily be calculated for $j \neq 0$. Regarding the determination of $R_1^{(i)}(0)$, we note that the left hand side of the above equation turns out to be zero irrespective of the value of $R_1^{(i)}(0)$. Therefore, to maintain the consistency between the two sides of eq. (26), we have

$$\frac{n^2}{2Z^2}\sum_{k=0}^{i-1} E_{i-k}\sum_{h=-1}^{+1} R_1^{(k)}(j+h)\, H_{n_1+j+h}(-h) + n\sum_{k=0}^{i-1} b_{i-k} R_1^{(k)}(j)$$

$$= \frac{n^3}{4Z^3}\sum_{l=-2}^{+2} R_1^{(i-1)}(j+l)\, C_{n_1+j+l}(-l). \tag{27}$$

For the time being we forget about the arbitrariness in $R_1^{(i)}(0)$'s and as particular solutions take them as follows :

$$R_1^{(i)}(0) = 0,\ i \neq 0;$$

$$R_1^{(0)}(0) = 1. \tag{28}$$

In a similar way, we obtain the solution of eq. (12) as

$$g_i(\rho_2) = \exp(-\rho_2/2)\exp(|m|/2)\sum_{j=-2i}^{+2i} R_2^{(i)}(j)\, L_{n_2+|m|+j}^{|m|}(\rho_2) \tag{29}$$

with

$$n_2 = n\beta_{20} - \frac{1}{2}(|m|+1). \tag{30}$$

The coefficients $R_2^{(i)}(j)$ $[-2i \leq j \leq 2i]$ are given by

$$R_2^{(i)}(j) = \frac{1}{j}\left[\frac{n^3}{4Z^3}\sum_{l=-2}^{+2} R_2^{(i-1)}(j+l)\, C_{n_2+j+l}(-l) - n\sum_{k=0}^{i-1} b_{i-k}\, R_2^{(k)}(j)\right.$$

$$\left. + \frac{n^2}{2Z^2}\sum_{k=0}^{i-1} E_{i-k}\sum_{h=-1}^{+1} R_2^{(k)}(j+h)\, H_{n_2+j+h}(-h)\right],\ j \neq 0;$$

$$R_2^{(i)}(0) = 0,\ i \neq 0;$$

$$R_2^{(0)}(0) = 1; \tag{31}$$

with

$$\frac{n^2}{2Z^2}\sum_{k=0}^{i-1} E_{i-k}\sum_{h=-1}^{+1} R_2^{(k)}(j+h) H_{n_2+j+h}(-h) - n\sum_{k=0}^{i-1} b_{i-k} R_2^{(k)}(j)$$

$$= -\frac{n^3}{4Z^3}\sum_{l=-2}^{+2} R_2^{(i-1)}(j+l)\, C_{n_2+j+l}(-l). \tag{32}$$

From eqs. (16), (30) and (6) it follows that

$$n = n_1 + n_2 + |m| + 1, \tag{33}$$

and thus n takes only integral values. Once the above relation is established, the i-th order energy correction (except $\mathcal{E}^i$) may be obtained from eqs. (27) and (32) as

$$E_i = \frac{1}{4Z} \sum_{l=-2}^{+2} \left[R_1^{(i-1)}(l) C_{n_1+l}(-l) - R_2^{(i-1)}(l) C_{n_2+l}(-l) \right] \cdot$$

$$- \frac{1}{2n} \sum_{k=1}^{i-1} E_{i-k} \sum_{h=-1}^{+1} \left[R_1^{(k)}(h) H_{n_1+h}(-h) + R_2^{(k)}(h) H_{n_2+h}(-h) \right]. \tag{34}$$

In view of eqs. (3), (7), (18), (25) and (29) the dressed wave function up to i-th order in λ may be written as

$$\Psi^{(i)} = A \sum_{l=0} \lambda^l \left[F^{(l)} \psi_0 + \sum_{r=0} \left(\sum_{j=-2r}^{+2r} R_1^{(r)}(j) L^{|m|}_{n_1+|m|+j}(\rho_1) \right. \right.$$

$$\left. \left. \sum_{j'=-2(l-r)}^{+2(l-r)} R_2^{(l-r)}(j') L^{|m|}_{n_2+|m|+j'}(\rho_2) \right) \right] \tag{35}$$

with

$$\psi_0 = L^{|m|}_{n_1+|m|}(\rho_1) L^{|m|}_{n_2+|m|}(\rho_2), \tag{36}$$

and

$$A = N \exp\left(-(\rho_1+\rho_2)/2\right) (\rho_1\rho_2)^{|m|/2} \exp(im\phi), \tag{37}$$

where N is the normalisation constant. This normalisation constant is to be determined from the normalisation condition

$$\int \Psi^{(i)^*} \Psi^{(i)} dv = 1. \tag{38}$$

This kind of normalisation is required by the particular type of collision problems involving dressed atomic wave functions in the presence of a laser field of our interest. As we have already pointed out in the introduction, our Stark states are not quite but almost stationary. An atom which is in such a state at some initial instant remains in it for a long period of time which is far far greater than the collision time of interest. Thus it is quite justified to normalise it in the usual way as is done in the case of bound states.

It is seen from eq. (35) that to maintain the proper normalisation condition of the dressed wave function, we have added parts proportional to the unperturbed wave function ψ_0 to every order correction to the eigenfunctions, $F^{(l)}$'s being the proportionality factors. The arbitrary nature of the coefficients $R_1^{(i)}(0)$ and $R_2^{(i)}(0)$ in eqs. (25) and (29) respectively has

been utilised successfully through these proportionality constants $F^{(l)}$. It is obvious that $F^{(0)} = 0$ and the other constants $F^{(l)}$ $(l \neq 0)$ can be determined from the normalisation of $\Psi^{(i)}$ [eq. (38)] retaining terms up to i-th order in λ. It may be noted that our choice of normalisation differs from the intermediate normalisation scheme which exploits the flexibility in the choice for the set of orthogonality integrals between the unperturbed and higher-order wave functions [10,11].

Thus, we have the following relation for the determination of $F^{(l)}$'s :

$$|N|^2 \frac{\pi n^3}{2Z^3} \sum_{p=0}^{i} \lambda^p \sum_{l=0}^{i} U(l,p) = 1, \tag{39}$$

where

$$U(l,p) = F^{(l)}F^{(p-l)}\left[(n_1+|m|)!\right]^3\left[(n_2+|m|)!\right]^3/(n_1!n_2!)+U_1+U_2+U_3, \tag{40a}$$

with

$$U_1 = \sum_{k=1}^{2}\left[(n_k+|m|)!\right]^3/n_k!\sum_{h=-1}^{+1}\left[(n_{3-k}+|m|+h)!\right]^3/(n_{3-k}+h)!\,H_{n_k}(h)$$

$$\times\left\{F^{(l)}R_{3-k}^{(p-l)}(h) + F^{(p-l)}R_k^{(l)}(h)\right\}, \tag{40b}$$

$$U_2 = \sum_{r=0}^{l}\sum_{r'=0}^{p-l}\left\{\sum_{j=-2r}^{+2r}R_1^{(r)}(j)\sum_{h=-1}^{+1}\left[(n_1+|m|+j+h)!\right]^3/(n_1+j+h)!\right.$$

$$\left.H_{n_1+j}(h)R_1^{(r')}(j+h)\right\}\sum_{j'=-2(l-r)}^{+2(l-r)}\left\{\left[(n_2+|m|+j')!\right]^3/(n_2+j')!\right.$$

$$\left.\times R_2^{(l-r)}(j')R_2^{(p-l-r')}(j')\right\}, \tag{40c}$$

$$U_3 = \sum_{r=0}^{l}\sum_{r'=0}^{p-l}\sum_{j=-2r}^{+2r}R_1^{(r)}(j)R_1^{(r')}(j)\left[(n_1+|m|+j)!\right]^3/(n_1+j)!\Big|$$

$$\sum_{j=-2(l-r)}^{+2(l-r)}R_2^{(l-r)}(j')\left\{\sum_{h=-1}^{+1}\left[(n_2+|m|+j'+h)!\right]^3/(n_2+j'+h)!\right.$$

$$\left.H_{n_2+j'}(h)R_2^{(p-l-r')}(j'+h)\right\} \tag{40d}$$

In obtaining the above equation we have used the orthogonality relation of the Laguerre polynomials $L_{p+|m|}^{|m|}(x)$ with respect to the weight $e^{-x}x^{|m|}$

$$\int e^{-x} x^{|m|} L^{|m|}_{p_1+|m|}(x)\, L^{|m|}_{p_2+|m|}(x)dx = 0, \qquad \text{if } p_1 \neq p_2;$$

$$= \left[(p_2 + |m|)\,!\right]^3 / p_2\,!\,, \qquad \text{if } p_1 = p_2. \tag{41}$$

The normalisation constant N can be obtained easily from eq. (39) putting $i = 0$ and then substituting $H_{n_1}(0)$ and $H_{n_2}(0)$ from eq. (21). Thus we have

$$N = \frac{1}{\sqrt{\pi}} \frac{Z^{3/2}}{n^2} \left[\frac{n_1\,!\; n_2\,!}{\left[(n_1+|m|)!\right]^3 \left[(n_2+|m|)!\right]^3} \right]^{1/2} \tag{42}$$

3. Application

This section contains a brief account of some application of the above theory to a neutral hydrogen atom placed in a uniform electric field. The outline of the calculations on energy corrections and wave function construction up to fourth order in the field intensity has been presented below.

First order perturbation :

The first order correction (apart from $\mathcal{E}$) to the unperturbed energy E_0 may be written down immediately from eq. (34) with $i = 1$

$$E_1 = 3nQ/2, \tag{43}$$

where $Q = n_1 - n_2$. In arriving at the result [eq. (43)] use of eq. (23) has been made for substituting $C_{n_1}(0)$ and $C_{n_2}(0)$.

From eq. (35) with $i = 1$, the eigenfunction up to first order is given by

$$\Psi^{(1)} = A\left[\psi_0 + \lambda \left\{F^{(1)}\psi_0 + P(1)\right\}\right], \tag{44a}$$

where

$$P(r) = \sum L^{|m|}_{n_{3-k}+|m|}(\rho_{3-k}) \sum^{+2r} R^{(r)}_k(j)\, L^{|m|}_{n_k+|m|+j}(\rho_k). \tag{44b}$$

The coefficients $R^{(1)}_1(j)$ and $R^{(1)}_2(j)$ with $-2 \leq j \leq 2$ and the proportionality factor $F^{(1)}$ in eq. (44) can be determined from the eqs. (26), (31) and (39) respectively with $i = 1$. These coefficients and the proportionality factor together with similar quantities for higher order perturbations are given in the appendix.

Second order perturbation :

Putting $i = 2$ in eq. (34) and making algebraical calculations with the help of eqs. (21), (23), (43) and (A1), we are led to the following second order energy correction (apart from $\mathcal{E}^2$)

$$E_2 = -n^4\left(17n^2 - 3Q^2 - 9m^2 + 19\right)/16. \tag{45}$$

Following eqs. (35) and (44) the eigenfunction up to second order in λ is given by

$$\Psi^{(2)} = \Psi^{(1)} + A\lambda^2\left[F^{(2)}\psi_0 + P(2) + T(1,1)\right], \tag{46a}$$

where

$$T(r,r') = \sum_{j=-2r}^{+2r} R_1^{(r)}(j)\, L^{|m|}_{n_1+|m|+j}(\rho_1) \sum_{j'=-2r'}^{+2r'} R_2^{(r')}(j')\, L^{|m|}_{n_2+|m|+j'}(\rho_2). \tag{46b}$$

Third order perturbation :

Following eq. (34) with $i = 3$ and making use of eqs. (21), (23), (43), (A1), (45) and (A3) the third order quota of energy (except $\mathcal{E}^3$) is reduced to the following compact form after some labour

$$E_3 = 3n^7Q\left(23n^2 - Q^2 + 11m^2 + 39\right)/32. \tag{47}$$

In view of eqs. (35) and (46) the normalised wave function up to third order in λ may be written down as

$$\Psi^{(3)} = \Psi^{(2)} + A\lambda^3\left[F^{(3)}\psi_0 + P(3) + T(1,2) + T(2,1)\right]. \tag{48}$$

Fourth order perturbation :

With the help of the expression for E_i as given in eq. (34) we write down the fourth order energy correction

$$E_4 = 1/4\left[\sum_{l=-2}^{+2}\left\{R_1^{(3)}(l)C_{n_1+l}(-l) - R_2^{(3)}(l)C_{n_2+l}(-l)\right\}\right]$$

$$-\frac{1}{2n}\sum_{k=1}^{3} E_{4-k}\sum_{h=-1}^{+1}\left\{R_1^{(k)}(h)H_{n_1+h}(-h) + R_2^{(k)}(h)H_{n_2+h}(-h)\right\}. \tag{49}$$

After a little bit of hard work using eqs. (21), (23), (43), (A1), (45), (A3), (47) and (A5) ultimately derive the fourth order term value of energy as given below

$$E_4 = -n^{10}\left(5487n^4 + 1806n^2Q^2 - 3402n^2m^2 + 35182n^2 + 147Q^4\right.$$

$$\left. - 1134Q^2m^2 + 5754Q^2 - 549m^4 - 8622m^2 + 16211\right)/1024. \tag{50}$$

The eigenfunction up to fourth order in λ may be given, with the help of eqs. (35) and (48), as

$$\Psi^{(4)} = \Psi^{(3)} + A\lambda^4\left[F^{(4)}\psi_0 + P(4) + T(1,3) + T(2,2) + T(3,1)\right]. \tag{51}$$

4. Results and discussion

The analytical expression for the perturbed energy for an arbitrary quantum state of the hydrogen atom up to fourth order in the field intensity is found to be identical with the results obtained by Alliluev and Malkin [6] who were able to eliminate all the mistakes from the previous calculations [5,16,17] quite successfully. Our energy expression through fourth order fully agrees with the corresponding expression recently obtained by Adams [4]. It may be pointed out that the energy expression up to fourth order for the ground state of the hydrogen atom, derived from the present calculation, has been checked and seen to be identical with the results of Mendelsohn [8] who has given expression for the energy up to 10th order.

Some numerical results of our calculations for the energy through fourth order in field intensity for the ground state and the excited state with $n = 5$, $n_1 = 3$, $n_2 = 0$, $m = 1$ of atomic hydrogen have been presented in Tables 1 and 2 for different field strengths.

In Table 1 our results for the ground state of hydrogen atom are given and compared with the results of Silverstone [7], Hehenberger *et al* [12] and Alexander [13]. It is noted that our results are in good agreement with the calculation of Silverstone [7] through fourth order.

Table 1. Energy calculated for the ground state of atomic hydrogen through fourth order in field intensity and compared with some previous results Atomic units are used throughout

Field strength	Present	Silverstone (1978)	Hehenberger *et al* (1974)	Alexander (1969)
0.06	–0 5088198875	–0.50918 (8)[a]	–0.509204	–0.5092
0 08	–0 5166752	–0.5167 (4)	–0.51756	–0.5175
0.09	–0.5218694305	–0 5219 (4)	–0 5224	–0.5222
0.10	–0 5280546875	–0 5281 (4)	–0.5275	–0.527
0.12	–0.5439182	–0 532 (2)	–0.5372	–0.536

[a] The number within parenthesis indicates the order of calculation.

It may be pointed out that his energy value calculated through second order for the field strength 0.12 a.u. is found to be in good agreement with our result –0.5324. But his result for the field strength 0.06 a.u. is slightly different from ours probably because of the difference in the order of calculation. Other results [12,13] are more or less in close agreement with ours. It may be pointed out that only two field strength values out of the five that we have considered are common with those of Damburg and Kolosov [14] and their energy values of these cases are in close agreement with ours.

Table 2 where the energy values for the excited state $n = 5$, $n_1 = 3$, $n_2 = 0$, $m = 1$ of hydrogen atom are given shows that our results through fourth order are in better agreement

with those of Silverstone [7] than with the results of Damburg and Kolosov [14] and Guschina and Nikulin [15] though differences are quite small. The energy calculated through second order for the field strength 0.00033061 a.u. is in complete agreement with the corresponding result of Silverstone [7]. In this particular case, the asymptotic series for the

Table 2. Energy calculated for the excited state with $n = 5$, $n_1 = 3$, $n_2 = 0$, $m = 1$ of atomic hydrogen through fourth order in field intensity and compared with some previous results. Atomic units are used throughout.

Field strength	Present	Silverstone (1978)	Damburg and Kolosov (1976)	Guschina and Nikulin (1975)
0.00015560	–0.0168601006	–0.01685516[12][a]	–0.0168552372	–0.0168401273
0.00019448	–0.0161914293	–0.0161821[12]	–0.0161793885	–0.01616271
0.00021393	–0.01587715	–0.015868[10]	–0.015860468	–0.0158429
0.00025282	–0.0152942808	–0.015294[5]	–0.015269204	–0.015255
0.00029172	–0.0147805445	–0.01478[4]	–0.014740243	–0.014735
0.00033061	–0.0143032911[b]	–0.01430[2]	–0.01424249	–0.01427

[a] Same as Table 1

[b] Only this result is given through second order and the reason for omission of higher order terms is discussed in Section 4.

energy expression starts increasing from the third order term. This is the reason why we have displayed the energy at this field strength only through second order (see also section 5).

5. Summary

A simple approach by perturbative method has been developed in the parabolic coordinate representation to study the Stark effect in hydrogen-like atoms to all orders and then application has been made to neutral hydrogen atom. It may be worth mentioning here that in this detailed analysis of the Stark effect equal importance has been given to the construction of dressed wave functions up to different higher order and the calculation of different order energy corrections.

Our perturbative method holds good only when the external electric field is sufficiently weak compared to the atomic field which depends on the quantum state of the atom, the field strength which is all right for the ground state may be too large for an excited state.

The salient feature of the present method is that the calculation of the eigenenergy expansion does not involve any type of successive approximations as used generally [5,6,18]. On the contrary, the different order energy corrections have been arrived at in a much simpler, straightforward and systematic way. This is because of the particular choice of the perturbation expansion of the separation parameters β_1 and β_2 [see eq. (7)] and also of the

scaling transformation involving the scaling parameter n [see eq. (10)]. However, it should be noted that the perturbation series for the Stark splitting of the levels do not converge in the strict sense, it is merely an asymptotic series. Thus, for a given field strength after a certain point in the series the terms go on increasing instead of decreasing. As the field strength increases this happens earlier. In other words, in order to have a good approximation one should stop at an appropriate point before terms start increasing.

Regarding the construction of the explicit dressed wave functions up to different higher order, it may be pointed out that considerable attention has been paid to meet the proper normalisation condition of these wave functions. An orthonormal set can easily be constructed from these normalised wave functions by following the well-known Schimidt procedure. It has been noted that the dressed ground state wave function of the hydrogen atom up to first order following from the present theory is identical with that given in Schiff [19].

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Appendix

In this mathematical appendix we determine the coefficients R_1 and R_2 and the proportionality factors F associated with different higher order dressed wave functions given by eqs. (44), (46), (48) and (51).

First-order perturbation :

The coefficients $R_1^{(1)}(j)$ $[-2 \le j \le 2]$ in eq. (44) can be determined from the general expression [eq. (26)]. Thus we get

$$R_1^{(1)}(2) = -n^3 C_{n_1}(2)/8, \tag{A1a}$$

$$R_1^{(1)}(1) = -n^3 C_{n_1}(1)/4 + n^2 E_1 H_{n_1}(1)/2, \tag{A1b}$$

$$R_1^{(1)}(-1) = n^3 C_{n_1}(-1)/4 - n^2 E_1 H_{n_1}(-1)/2, \tag{A1c}$$

$$R_1^{(1)}(-2) = n^3 C_{n_1}(-2)/8. \tag{A1d}$$

It is seen that $R_1^{(1)}(-1)$ and $R_1^{(1)}(-2)$ can be obtained easily from $R_1^{(1)}(1)$ and $R_1^{(1)}(2)$ respectively, by changing their overall sign and also changing the sign of the argument of the C_{n_1}'s and H_{n_1}'s. The same is true for $R_2^{(1)}(-1)$ and $R_2^{(1)}(-2)$ while $R_2^{(1)}(1)$ and $R_2^{(1)}(2)$ are given by expressions similar to eqs. (A1b) and (A1a) with n_1 and n replaced by n_2 and $-n$, respectively, as is evident from eq. (31). Thus, while considering higher order perturbations we shall give explicit expressions for only the coefficients R_j of positive argument.

The proportionality factor $F^{(1)}$ in eq. (44) can be determined directly from eq. (39) with $i = 1$ and it is given by

$$F^{(1)} = -\frac{1}{2n} \sum_{k=1}^{\infty} B_1(k), \tag{A2a}$$

where

$$B_1(k) = \sum_{j=-1}^{2} R_k^{(1)}(j) H_{n_k}(j) G_j(n_k), \tag{A2b}$$

with

$$G_1(n_k) = (n_k + |m| + 1)^3 / (n_k + 1); \quad G_{-1}(n_k) = n_k / (n_k + |m|)^3. \tag{A2c}$$

Second-order perturbation :

Following eq. (26) the coefficients $R_1^{(2)}(j)$ $[-4 \le j \le 4]$ associated with $\Psi^{(2)}$ in eq. (46) can be determined from eq. (26). Thereby we have

$$R_1^{(2)}(4) = -n^3 R_1^{(1)}(2) C_{n_1+2}(2)/16,$$

$$R_1^{(2)}(3) = -R_1^{(1)}(2)\left[n^3 C_{n_1+2}(1)/4 - n^2 E_1 H_{n_1+2}(1)/2\right]/3$$

$$- n^3 R_1^{(1)}(1) C_{n_1+1}(2)/12,$$

$$R_1^{(2)}(2) = -3n^3(n+2)R_1^{(1)}(2)/2 - R_1^{(1)}(1)\left[n^3 C_{n_1+1}(1)/4\right.$$

$$\left. - n^2 E_1 H_{n_1+1}(1)/2\right]/2,$$

$$R_1^{(2)}(1) = -R_1^{(1)}(2)\left[n^3 C_{n_1+2}(-1)/4 - n^2 E_1 H_{n_1+2}(-1)/2\right]$$

$$-3n^3(n+1)R_1^{(1)}(1)/2 - n^3 R_1^{(1)}(-1)C_{n_1-1}(2)/4 + n^2 E_2 H_{n_1}(1)/2 \qquad \text{(A3)}$$

From eq. (39) with $i = 2$, we can express the proportionality factor $F^{(2)}$ as

$$F^{(2)} = -\frac{1}{4n}\sum_{k=1}^{2} B_2(k), \qquad \text{(A4a)}$$

where

$$B_2(k) = F^{(1)}B_1(k) + \sum_{J=-1}^{+1}\left[G_{2J}(n_k)\left\{\left[R_k^{(1)}(2J)\right]^2(2n+4J)\right.\right.$$

$$\left. + 2R_k^{(1)}(2J)R_k^{(1)}(J)H_{n_k+J}(J)\right\} + G_J(n_k)\left\{\left[R_k^{(1)}(J)\right]^2(2n+2J)\right.$$

$$\left.\left. + 2R_k^{(2)}(J)H_{n_k}(J)\right\}\right], \qquad \text{(A4b)}$$

$$G_2(n_k) = G_1(n_k)\left(n_k+|m|+2\right)^3/\left(n_k+2\right), \qquad \text{(A4c)}$$

$$G_{-2}(n_k) = G_{-1}(n_k)\left(n_k-1\right)/\left(n_k+|m|-1\right)^3.$$

$F^{(1)}$, $B_1(k)$, $G_1(n_k)$ and $G_{-1}(n_k)$ in the above equations are given by eqs (A2)

Third-order perturbation :

In view of eqs. (26) and (39), the coefficients $R_1^{(3)}(j)$ $[-6 \le j \le 6]$ and the factor $F^{(3)}$ in eq. (48) can be determined respectively. Thus we get

$$R_1^{(3)}(6) = -n^3 R_1^{(2)}(4) C_{n_1+4}(2)/24,$$

$$R_1^{(3)}(5) = -R_1^{(2)}(4)\left[n^3 C_{n_1+4}(1)/4 - n^2 E_1 H_{n_1+4}(1)/2\right]/5$$

$$- n^3 R_1^{(2)}(3) C_{n_1+3}(2)/20,$$

Appendix

In this mathematical appendix we determine the coefficients R_1 and R_2 and the proportionality factors F associated with different higher order dressed wave functions given by eqs. (44), (46), (48) and (51).

First-order perturbation :

The coefficients $R_1^{(1)}(j)$ $[-2 \le j \le 2]$ in eq. (44) can be determined from the general expression [eq. (26)]. Thus we get

$$R_1^{(1)}(2) = -n^3 C_{n_1}(2)/8, \tag{A1a}$$

$$R_1^{(1)}(1) = -n^3 C_{n_1}(1)/4 + n^2 E_1 H_{n_1}(1)/2, \tag{A1b}$$

$$R_1^{(1)}(-1) = n^3 C_{n_1}(-1)/4 - n^2 E_1 H_{n_1}(-1)/2, \tag{A1c}$$

$$R_1^{(1)}(-2) = n^4 C_{n_1}(-2)/8. \tag{A1d}$$

It is seen that $R_1^{(1)}(-1)$ and $R_1^{(1)}(-2)$ can be obtained easily from $R_1^{(1)}(1)$ and $R_1^{(1)}(2)$ respectively, by changing their overall sign and also changing the sign of the argument of the C_{n_1}'s and H_{n_1}'s. The same is true for $R_2^{(1)}(-1)$ and $R_2^{(1)}(-2)$ while $R_2^{(1)}(1)$ and $R_2^{(1)}(2)$ are given by expressions similar to eqs. (A1b) and (A1a) with n_1 and n replaced by n_2 and $-n$, respectively, as is evident from eq. (31). Thus, while considering higher order perturbations we shall give explicit expressions for only the coefficients R_j of positive argument

The proportionality factor $F^{(1)}$ in eq. (44) can be determined directly from eq. (39) with $i = 1$ and it is given by

$$F^{(1)} = -\frac{1}{2n} \sum_{k=1}^{2} B_1(k), \tag{A2a}$$

where

$$B_1(k) = \sum_{j=-1}^{+1} R_k^{(1)}(j) H_{n_k}(j) G_j(n_k), \tag{A2b}$$

with

$$G_1(n_k) = \left(n_k + |m| + 1\right)^3 / \left(n_k + 1\right) ; \; G_{-1}(n_k) = n_k / \left(n_k + |m|\right)^3. \tag{A2c}$$

Second-order perturbation :

Following eq. (26) the coefficients $R_1^{(2)}(j)$ $[-4 \le j \le 4]$ associated with $\Psi^{(2)}$ in eq. (46) can be determined from eq. (26). Thereby we have

$$R_1^{(2)}(4) = -n^3 R_1^{(1)}(2) C_{n_1+2}(2)/16,$$

$$R_1^{(2)}(3) = -R_1^{(1)}(2)\left[n^3 C_{n_1+2}(1)/4 - n^2 E_1 H_{n_1+2}(1)/2\right]/3$$

$$- n^3 R_1^{(1)}(1) C_{n_1+1}(2)/12,$$

$$R_1^{(2)}(2) = -3n^3(n+2)R_1^{(1)}(2)/2 - R_1^{(1)}(1)\left[n^3 C_{n_1+1}(1)/4\right.$$

$$\left. - n^2 E_1 H_{n_1+1}(1)/2\right]/2,$$

$$R_1^{(2)}(1) = -R_1^{(1)}(2)\left[n^3 C_{n_1+2}(-1)/4 - n^2 E_1 H_{n_1+2}(-1)/2\right]$$

$$-3n^3(n+1)R_1^{(1)}(1)/2 - n^3 R_1^{(1)}(-1)C_{n_1-1}(2)/4 + n^2 E_2 H_{n_1}(1)/2. \quad \text{(A3)}$$

From eq. (39) with $i = 2$, we can express the proportionality factor $F^{(2)}$ as

$$F^{(2)} = -\frac{1}{4n}\sum_{k=1}^{2} B_2(k), \quad \text{(A4a)}$$

where

$$B_2(k) = F^{(1)}B_1(k) + \sum_{j=-1}\left[G_{2j}(n_k)\left\{\left[R_k^{(1)}(2j)\right]^2(2n+4j)\right.\right.$$

$$\left. + 2R_k^{(1)}(2j)R_k^{(1)}(j)H_{n_k+j}(j)\right\} + G_j(n_k)\left\{\left[R_k^{(1)}(j)\right]^2(2n+2j)\right.$$

$$\left.\left. + 2R_k^{(2)}(j)H_{n_k}(j)\right\}\right], \quad \text{(A4b)}$$

$$G_2(n_k) = G_1(n_k)\left(n_k+|m|+2\right)^3/\left(n_k+2\right), \quad \text{(A4c)}$$

$$G_{-2}(n_k) = G_{-1}(n_k)\left(n_k-1\right)/\left(n_k+|m|-1\right)^3.$$

$F^{(1)}$, $B_1(k)$, $G_1(n_k)$ and $G_{-1}(n_k)$ in the above equations are given by eqs (A2).

Third-order perturbation :

In view of eqs. (26) and (39), the coefficients $R_1^{(3)}(j)$ $[-6 \le j \le 6]$ and the factor $F^{(3)}$ in eq. (48) can be determined respectively. Thus we get

$$R_1^{(3)}(6) = -n^3 R_1^{(2)}(4) C_{n_1+4}(2)/24,$$

$$R_1^{(3)}(5) = -R_1^{(2)}(4)\left[n^3 C_{n_1+4}(1)/4 - n^2 E_1 H_{n_1+4}(1)/2\right]/5$$

$$- n^3 R_1^{(2)}(3) C_{n_1+3}(2)/20,$$

$$R_1^{(3)}(4) = -R_1^{(2)}(4)\left[n^3 C_{n_1+4}(0)/4 - n^2 E_1 H_{n_1+4}(0)/2 - b_1 n\right]/4$$

$$- R_1^{(2)}(3)\left[n^3 C_{n_1+3}(1)/4 - n^2 E_1 H_{n_1+3}(1)/2\right]/4$$

$$- n^3 R_1^{(2)}(2) C_{n_1+2}(2)/16,$$

$$R_1^{(3)}(3) = -R_1^{(2)}(4)\left[n^3 C_{n_1+4}(-1)/4 - n^2 E_1 H_{n_1+4}(-1)/2\right]/3$$

$$-R_1^{(2)}(3)\left[n^3 C_{n_1+3}(0)/4 - n^2 E_1 H_{n_1+3}(0)/2 - b_1 n\right]/3$$

$$-R_1^{(2)}(2)\left[n^3 C_{n_1+2}(1)/4 - n^2 E_1 H_{n_1+2}(1)/2\right]/3$$

$$+ n^2 E_2 H_{n_1+2}(1) R_1^{(1)}(2)/6 - n^3 R_1^{(2)}(1) C_{n_1+1}(2)/12,$$

$$R_1^{(3)}(2) = -R_1^{(2)}(3)\left[n^3 C_{n_1+3}(-1)/4 - n^2 E_1 H_{n_1+3}(-1)/2\right]/2$$

$$-R_1^{(2)}(2)\left[n^3 C_{n_1+2}(0)/4 - n^2 E_1 H_{n_1+2}(0)/2 - b_1 n\right]/2$$

$$-R_1^{(2)}(1)\left[n^3 C_{n_1+1}(1)/4 - n^2 E_1 H_{n_1+1}(1)/2\right]/2$$

$$+ n^2 E_2\left[R_1^{(1)}(2) H_{n_1+2}(0) + R_1^{(1)}(1) H_{n_1+1}(1)\right]/4$$

$$-n^3 R_1^{(2)}(4) C_{n_1+4}(-2)/8 + b_2 n R_1^{(1)}(2)/2,$$

$$R_1^{(3)}(1) = -R_1^{(2)}(2)\left[n^3 C_{n_1+2}(-1)/4 - n^2 E_1 H_{n_1+2}(-1)/2\right]$$

$$-R_1^{(2)}(1)\left[n^3 C_{n_1+1}(0)/4 - n^2 E_1 H_{n_1+1}(0)/2 - b_1 n\right]$$

$$-n^3\left[R_1^{(1)}(3) C_{n_1+3}(-2) + R_1^{(1)}(-1) C_{n_1-1}(2)\right]/4$$

$$+n^2 E_2\left[R_1^{(1)}(2) H_{n_1+2}(-1) + R_1^{(1)}(1) H_{n_1+1}(0)\right]/2$$

$$+b_2 n R_1^{(1)}(1) + n^2 E_3 H_{n_1}(1), \tag{A5}$$

and

$$F^{(3)} = -F^{(1)} F^{(2)} + \frac{1}{2n}\sum_{k=1} B_3(k), \tag{A6a}$$

where

$$B_3(k) = F^{(2)}B_1(k) + B_1(3-k)D(k) + \sum_{j=-1} G_{3j}(n_k)R_k^{(1)}(2j)R_2^{(2)}(3j)$$

$$H_{n_k+2j}(j) + G_{2j}(n_k)\left[H_{n_k+j}(j)R_k^{(1)}(j) + (2n+4j)R_k^{(1)}(2j)\right]$$

$$R_k^{(2)}(2j) + G_j(n_k)\left[R_k^{(2)}(j)\times\left\{H_{n_k+2j}(-j)R_k^{(1)}(2j) + (2n+2j)R_k^{(1)}(j)\right\}\right.$$

$$\left. + H_{n_k}(j)\left\{R_k^{(3)}(j) + F^{(1)}R_k^{(2)}(j)\right\}\right]. \qquad \text{(A6b)}$$

The factors $D(k)$, $G_3(n_k)$ and $G_{-3}(n_k)$ occurring in the above equation are given by

$$D(k) = \sum_{j=-2}^{+2}\left[R_k^{(1)}(j)\right]^2 G_j(n_k), \qquad \text{(A6c)}$$

$$G_3(n_k) = G_2(n_k)\left[n_k + |m| + 3\right]^3/(n_k+3), \qquad \text{(A6d)}$$

$$G_{-3}(n_k) = G_{-2}(n_k)\,(n_k-2)/\left[n_k + |m| - 2\right]^3.$$

Fourth–order perturbation :

The coefficients $R_1^{(4)}(j)$ $[-8 \le j \le 8]$ and the proportionality factor $F^{(4)}$ associated with $\Psi^{(4)}$ in eq. (51) can be determined from eqs. (26) and (39) respectively. These quantities are given below

$$R_1^{(4)}(8) = -n^3R_1^{(3)}(6)\,C_{n_1+6}(2)/32,$$

$$R_1^{(4)}(7) = -R_1^{(3)}(6)\left[n^3C_{n_1+6}(1)/4 - n^2E_1H_{n_1+6}(1)/2\right]/7$$

$$-n^3R_1^{(3)}(5)C_{n_1+5}(2)/28,$$

$$R_1^{(4)}(6) = -R_1^{(3)}(6)\left[n^3C_{n_1+6}(0)/4 - n^2E_1H_{n_1+6}(0)/2 - b_1n\right]/6$$

$$-R_1^{(3)}(5)\left[n^3C_{n_1+5}(1)/4 - n^2E_1H_{n_1+5}(1)/2\right]/6$$

$$-n^3R_1^{(3)}(4)C_{n_1+4}(2)/24,$$

$$R_1^{(4)}(5) = -R_1^{(3)}(6)\left[n^3C_{n_1+6}(-1)/4 - n^2E_1H_{n_1+6}(-1)/2\right]/5$$

$$-n^3R_1^{(3)}(3)C_{n_1+3}(2)/20 - R_1^{(3)}(5)\left[n^3C_{n_1+5}(0)/4\right.$$

$$-n^2E_1H_{n_1+5}(0)/2-b_1n\Big]/5 - R_1^{(3)}(4)\Big[n^3C_{n_1+4}(1)/4$$

$$-n^2E_1H_{n_1+4}(1)/2\Big]/5 + n^2E_2R_1^{(2)}(4)H_{n_1+4}(1)/10,$$

$$R_1^{(4)}(4) = -n^3R_1^{(3)}(6)C_{n_1+6}(-2)/16 - R_1^{(3)}(5)\Big[n^3C_{n_1+5}(-1)/4$$

$$-n^2E_1H_{n_1+5}(-1)/2\Big]/4 - R_1^{(3)}(4)\Big[n^3C_{n_1+4}(0)/4$$

$$-n^2E_1H_{n_1+4}(0)/2 - b_1n\Big]/4 - R_1^{(3)}(3)\Big[n^3C_{n_1+3}(1)/4$$

$$-n^2E_1H_{n_1+3}(1)/2\Big]/4 - n^3R_1^{(3)}(2)C_{n_1+2}(2)/16$$

$$+R_1^{(2)}(4)\Big[n^2E_2H_{n_1+4}(0) + b_2n\Big]/4 + n^2E_2R_1^{(2)}H_{n_1+3}(1)/8,$$

$$R_1^{(4)}(3) = -n^3R_1^{(3)}(5)C_{n_1+5}(-2)/12 - R_1^{(3)}(4)\Big[n^3C_{n_1+4}(-1)/4$$

$$-n^2E_1H_{n_1+4}(-1)/2\Big]/3 - R_1^{(3)}(3)\Big[n^3C_{n_1+3}(0)/4 - n^2E_1H_{n_1+3}(0)/2$$

$$-b_1n\Big]/3 - R_1^{(3)}(2)\Big[n^3C_{n_1+2}(1)/4 - n^2E_1H_{n_1+2}(1)/2\Big]/3$$

$$-n^3R_1^{(3)}(1)C_{n_1+1}(2)/12 + n^2E_2\Big[R_1^{(2)}(4)H_{n_1+4}(-1)$$

$$+R_1^{(2)}(2)H_{n_1+2}(1)\Big]/6 + R_1^{(2)}(3)\Big[n^2E_2H_{n_1+3}(0)/2 + b_2n\Big]/3$$

$$+n^2E_3R_1^{(1)}(2)H_{n_1+2}(1)/6,$$

$$R_1^{(4)}(2) = -n^3R_1^{(3)}(4)C_{n_1+4}(-2)/8 - R_1^{(3)}(3)\Big[n^3C_{n_1+3}(-1)/4$$

$$-n^2E_1H_{n_1+3}(-1)/2\Big]/2 - R_1^{(3)}(2)\Big[n^3C_{n_1+2}(0)/4 - n^2E_1H_{n_1+2}(0)/2$$

$$-b_1n\Big]/2 - R_1^{(3)}(1)\Big[n^3C_{n_1+1}(1)/4 - n^2E_1H_{n_1+1}(1)/2\Big]/2$$

$$+n^2E_3R_1^{(1)}(1)H_{n_1+1}(1)/4 + n^2E_2\Big[R_1^{(2)}(3)H_{n_1+3}(-1)$$

$$+R_1^{(2)}(1)H_{n_1+1}(1)\Big]/4 + R_1^{(2)}(2)\Big[\frac{n^2}{2}E_2H_{n_1+2}(0) + b_2n\Big]/2$$

$$+R_1^{(1)}(2)\Big[\frac{n^2}{2}E_3H_{n_1+2}(0) + b_3n\Big]/2,$$

$$R_1^{(4)}(1) = -n^3 R_1^{(3)}(3) C_{n_1+3}(-2)/4 - R_1^{(3)}(2)\left[n^3 C_{n_1+2}(-1)/4 - n^2 E_1 H_{n_1+2}(-1)/2\right] - R_1^{(3)}(1)\left[n^3 C_{n_1+1}(0)/4 - n^2 E_1 H_{n_1+1}(0)/2 - b_1 n\right] - n^3 R_1^{(3)}(-1) C_{n_1-1}(2)/4 + n^2 E_2 R_1^{(2)}(2) H_{n_1+2}(-1)/2 + R_1^{(2)}(1)\left[n^2 E_2 H_{n_1+1}(0)/2 + b_2 n\right] + n^2 E_3 R_1^{(1)}(2) H_{n_1+2}(-1)/2 + R_1^{(1)}(1)\left[n^2 E_3 H_{n_1+1}(0)/2 + b_3 n\right] + n^2 E_4 H_{n_1}(1)/2, \quad \text{(A7)}$$

and

$$F^{(4)} = -F^{(1)} F^{(3)} - [F^{(2)}]^2/2 - \frac{1}{4n} \sum_{k=1}^{\infty} B_4(k), \quad \text{(A8a)}$$

where

$$B_4(k) = 4B_1(3-k) \sum^{+2} R_k^{(1)}(j) R_k^{(2)}(j) G_j(n_k) + \sum_{j=-1}^{+1} \left[D(k) D_1(j,k) + D_2(j,k)\right]. \quad \text{(A8b)}$$

The functions $D_1(j,k)$ and $D_2(j,k)$ in the above equation are given by

$$D_1(j,k) = G_{2j}(n_{3-k}) R_{3-k}^{(1)}(2j)\left[H_{n_{3-k}+2j}(0) R_{3-k}^{(1)}(2j) + H_{n_{3-k}+j}(j) R_{3-k}^{(1)}(j)\right] + G_j(n_{3-k})\left[\left\{H_{n_{3-k}+2j}(-j) R_{3-k}^{(1)}(2j) + H_{n_{3-k}+j}(0) R_{3-k}^{(1)}(j)\right\} R_{3-k}^{(1)}(j) + 2H_{n_{3-k}}(j) R_{3-k}^{(2)}(j)\right], \quad \text{(A8c)}$$

$$D_2(j,k) = 2H_{n_k}(j) G_j(n_k)\left[R_k^{(4)}(j) + F^{(1)} R_k^{(3)}(j) + F^{(2)} R_k^{(2)}(j) + F^{(3)} R_k^{(1)}(j) + G_{4j}(n_k) R_k^{(-1)}(4j)\left[(2n+8j) R_k^{(-1)}(4j) + H_{n_k+3j}(j) R_k^{(-1)}(3j)\right] + G_{3j}(n_k)\left[H_{n_k+2j}(j)\left\{R_k^{(2)}(2j) R_k^{(2)}(3j) + 2R_k^{(1)}(2j) R_k^{(3)}(3j)\right\} + H_{n_k+4j}(-j) R_k^{(2)}(4j) R_k^{(2)}(3j) + (2n+6j)\left(R_k^{(2)}(3j)\right)^2\right] + G_{2j}(n_k)\left[(2n+4j)\left\{\left(R_k^{(2)}(2j)\right)^2 + 2R_k^{(1)}(2j) R_k^{(3)}(2j)\right\} + \left\{2R_k^{(1)}(j) R_k^{(3)}(2j) + R_k^{(2)}(j) R_k^{(2)}(2j)\right\} H_{n_k+j}(j)\right.$$

$$+ H_{n_k+3j}(-j)R_k^{(2)}(3j)R_k^{(2)}(2j)\Big] + G_j(n_k)\Big[H_{n_k+2j}(-j)$$

$$\Big\{R_k^{(2)}(2j)R_k^{(2)}(j) + 2R_k^{(1)}(2j)R_k^{(3)}(j)\Big\} + (2n+2j)$$

$$\Big\{\Big(R_k^{(2)}(j)\Big)^2 + 2R_k^{(1)}(j)R_k^{(3)}(j)\Big\}\Big]. \qquad \text{(A8d)}$$

The two factors $G_4(n_k)$ and $G_{-4}(n_k)$ are of the following form

$$G_4(n_k) = G_3(n_k)\big[n_k + |m| + .4\big]^3_{\bullet}\big/\big(n_k + 4\big),$$

$$G_{-4}(n_k) = G_{-3}(n_k)\big(n_k - 3\big)\big/\big[n_k + |m| - 3\big]^3. \qquad \text{(A8e)}$$